Wood Science and Technology

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--Manuscript Draft--

Manuscript Number:	
Full Title:	Green biorefinery of larch wood biomass with obtaining of bioactive compounds, functional polymers and nanoporous materials
Article Type:	Original Article
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Green biorefinery of larch wood biomass with obtaining of bioactive compounds, functional polymers and nanoporous materials

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Abstract

The first green biorefinery of larch wood based on new methods of biomass fractionation on dihydroquercitin (DHQ), arabinogalactan (AG), microcrystalline cellulose (MCC) and soluble lignin (SL) is reported. The new green method of one-step isolation of DHQ and AG from larch wood by ethanol-water solution is described. The first results of kinetic studies and optimization of the process of extracted larch wood peroxide fractionation on MCC and SL in acetic acid – water medium in the presence of green TiO2 catalyst are presented. The products obtained from larch wood were characterized by FTIR, SEM, AFM, XRD and chemical methods. The scheme of larch wood biorefinery is suggested which integrates the described processes of biomass fractionation on DHQ, AG, MCC, SL and the yearly developed methods of polysaccharides processing to bioactive cupper and amino acid – containing sulfated polymers along with the methods of nanoporous materials synthesis from lignin. All these methods use such non-toxic and less-toxic reagents, as water, ethanol, hydrogen peroxide, acetic acid, sulfamic acid, urea.

Introduction

Annual growth of plant biomass far exceeds the requirements of mankind for fuel and chemical products (Naik et al. 2010; Davis et al. 2014). Actually, from the components of plant biomass it is possible to obtain the entire range of products of modern petrochemical synthesis, as well as unique natural compounds, in particular physiologically active substances. Lignocellulosic biomass mainly consists of cellulose, hemicelluloses and lignin (Sjostrom 1993; Rowell 2012). These plant polymers are structured in plant cells in a complex way and the lignocellulosic biomass is quite resistant to chemical reagents and enzymes (Pandey 2015; Furkan et al. 2015). Therefore, in industrial pulp and hydrolysis processes the chemically aggressive and environmentally hazardous reagents, elevated temperatures and pressures are used (Sixta 2006).

Traditional catalysts for biomass transformation processes are corrosive and environmentally hazardous mineral acids. The problems of their use are associated with the occurrence of side reactions and the difficulties in separation of target products and catalyst from the reaction medium.

Current research trends in the development of new efficient processes for the conversion of lignocellulosic biomass to valuable chemicals, functional polymers and bioethanol are associated with the use of solid catalysts and "green" reagents (Fang et al. 2016; Serrano-Ruiz and Dumesic 2011; Bessone et al. 2014). To increase the biomass reactivity and the area of its contact with solid catalyst, as well as to reduce the diffusion limitations in heterogeneous catalytic processes of biomass conversion, the various activation methods (mechanical, mechanochemical, chemical, etc.) are used (Ramos 2003; Zeng et al. 2009). The principle possibility of application of solid acid and bifunctional catalysts for hydrolysis of cellulose in aqueous medium was shown (Hu et al. 2015;

Gliozzi et al. 2014; Ishida et al. 2014; Liu et al. 2015). In recent year, studies are actively conducted on development the integrated technologies of biomass complex processing (Cherubini et al. 2009; Ed de Long et al. 2013; Zhang et al. 2016; Zhang et al. 2015).

Promising integrated processes for biomass conversion include, as a key step, its fractionation on cellulose, sugars and lignin, from which the other various chemicals are obtained (Dagle et al. 2016; Daijang and Chen 2014; Xu et al. 2016, Zhang et al. 2015).

The authors suggested to use one-stage catalytic processes of wood fractionation in the medium "hydrogen peroxide-acetic acid-water" (Kuznetsov et al. 2008; Kuznetsov et al. 2009; Kuznetsov et al. 2015) and in supercritical ethanol (Baryshnikov et al. 2014; Sharypov et al. 2015).

Since the wood species differ in their chemical composition, and therefore in the composition of the products of their processing, an important task is to develop the optimal green methods for transformation the biomass of the most common tree species to the valuable chemicals, biofuels and functional polymers.

Larch is the predominant coniferous species in the forests of Siberia, Canada and North America. The high density of the wood and the large amount of extractives complicate the use of larch wood in the pulp and hydrolysis industries. The most effective way of the use of larch biomass is its complex chemical processing with obtaining valuable physiologically active compounds and new functional polymers (Horhammer et al. 2014).

Most of the works published in recent years are devoted to the extractive isolation of bioactive dihydroquercetin and arabinogalactan from larch wood (Ravber et al. 2015; Troshina and Roshchin 2014; Ma et al. 2012).

The task of the present study is to develop a new approach to the complex environmetally safe processing of larch wood, based on the integration in a single technological cycle the new "green" methods of biomass components conversion to a wide range of demanded products.

Materials and methods

Air-dry sawdust (fraction 2-5 mm) of larch wood (*Larix sibirica Ledeb*) harvested in the forest area near Krasnoyarsk city was used as initial raw material. Wood composition (wt%): cellulose 41.2, lignin 28.1, hemicellulose 26.4 (including arabinogalactan 19.9), dihydroquercetin 2.0, ash 1,0.

Isolation of dihydroquercetin and arabinogalactan

The flask volume of 2 liters, equipped with a reflux condenser was charged with 100 g larch wood, poured 1.5l of water or 5–25% aqueous solution of ethanol (special purity, Sigma Tech, Russia) and heated on a steam bath for 2 hours. Then solution was separated from the wood and concentrated under vacuum on a rotary evaporator to 60–80ml, while stirring it diluted with 300 ml of ethanol. The precipitated AG was separated by filtration, washed on a filter with 40-50 ml of ethanol and dried at room temperature. The mother solution in the amount of 400–430 ml remaining after separation of AG, was concentrated under vacuum until complete removal of the solvent. Then to the flask with a dry residue was added 350–400 ml of 96% ethanol, clarified with activated carbon and heated on a steam bath for 10 minutes and filtered through a filter alumina oxide. The resulting solution was concentrated under vacuum on a rotary evaporator to completely remove ethanol. DHQ was obtained in the form of loose powder of light yellow color.

Peroxide fractionation of larch wood

Catalytic delignification of wood sawdust by H_2O_2 was carried out as in (Kuznetsov et al. 2013) using 250 cm^3 glass reactor equipped with mechanical stirrer, reflux condenser and thermometer. Wood sawdust (10 g) was

placed in the glass reactor. Then, a mixture of glacial acetic acid, hydrogen peroxide (all of special purity, Sigma Tech, Russia), distilled water and commercial TiO_2 (analytical purity, DuPont, USA) was added. The reaction mixture was vigorously stirred (700 rpm) at selected temperature (70–100 °C) during 1–4 h. Composition of the reaction mixture was varied in the following range: hydrogen peroxide 3–7 wt%, acetic acid 15–40 wt%, liquid/wood ratio (LWR) 10–15. Concentration of TiO_2 catalyst was at 1 wt%. TiO_2 has an average particle size of about 10 microns, rutile phase composition and BET surface area of 3 m^2/g. When the reaction was completed, the solid product was separated under vacuum using Buchner funnel and drying at 105 °C until constant weight.

The residual lignin content in cellulosic product was used to evaluate the delignification activity of TiO_2 catalyst. The cellulosic product yield was estimated by gravimetric method and calculated as follows: $Y = (m/m_o) \times 100$, where Y – yield of cellulosic product, wt%; m – weight of abs. dry cellulosic product, g; m_o – weight of abs. dry wood, g.

Analytical methods

The content of cellulose, hemicelluloses and lignin in solid products was defined chemical methods, generally accepted in wood chemistry (Sjoöstroöm and Alern 1999).

X-ray diffraction analysis of cellulose products was carried out on PANalyticalX'Pert Pro diffractometer using Cu-Ka source (A = 0,154 nm) in the 2θ range 5–70 ° and scanning step width of 0.01 °/scan. The samples of cellulose were analyzed by the powder method in cuvette with 25 mm diameter. Crystallinity index (CI) was calculated from the ratio of the height between the intensity of the crystalline peak and total intensity after subtraction of the background signal (Park et al. 2010):

$$CI = (I_{002} - I_{AM}) / (I_{002}),$$

where I_{002} –is the height of the 002 peak; I_{AM} – is the height of the minimum between the 002 and the 101 peaks.

Infrared spectroscopy analysis (FTIR) was carried out in transmission mode. Samples of cellulose (4 mg for each) were prepared in pellet with matrix KBr. The spectra were recorded with Bruker Tensor – 27 in the range4000–400 cm^{-1} wavelength. Spectral data were processed by the program OPUS/YR (version 2.2).

The electron images were obtained with scanning electron microscope TM-1000 HITACHI (Japan) with accelerating potential 15 kV. Samples were coated on carbon support.

AFM images were obtained with scanning probing multimode microscope Solver P47 (NT-MDT, Moscow). Transparent films of samples were prepared by evaporation of their water solutions on flat support made from glass. The rate of scanning was 1–2 Hz and the number of points on scanning area 256 × 256 or 512 × 512.

Results and discussion

Extraction of bioactive dihydroquercitin and arabinogalactan from larch wood

Bioactive dihydroquercetin (DHQ) and arabinogalactan (AG) are increasingly used in medicine, pharmaceutical and food industries (Babkin et al. 1997; Goellner et al. 2011). AG is a promising precursor for synthesis of new bioactive polymers (Medvedeva et al. 2003).

Larch wood contains to 2,5 % wt. of flavonoids and to 20 % wt. polysaccharide arabinogalactan. The content of DHQ (3,3′,4′,5,7 – pentaoxyflavone) reaches 90 % from the sum of flavonoids. AG is usually obtained by water extraction of larch wood (Medvedeva et al. 2003). The known methods of DHQ isolation are based on larch wood extraction by organic solvents, mainly by ethylacetate and acetone (Babkin et al. 2000; Kislitsin and Mal'chikov 2009; Gavrilov 2009). Oganic solvents extract together with DHQ resinous substance which contaminate the dihydroquercitin. In particular, the extraction of larch wood by 80-86% ethanol significantly

contaminated DHQ with resinous substances and complicated and lengthy purification was required to obtain the pure product (Gavrilov 2009).

We developed the new green method of one-step isolation of DHQ and AG by water-ethanol extraction on larch wood. This method provides the simultaneous production of DHQ and AG, which are not contaminated with resinous substances.

The effect of ethanol concentration in water solution on the yield of DHQ and AG from larch wood was studied. It was found that the maximum yield of DHQ (1.81% wt.) corresponds to the ethanol concentration of 15% and it does not increase with further rise of the ethanol content in the solution (Fig. 1a). However, the yield of AG decreases with the growth of ethanol concentration in water over 10% (Fig.1b).

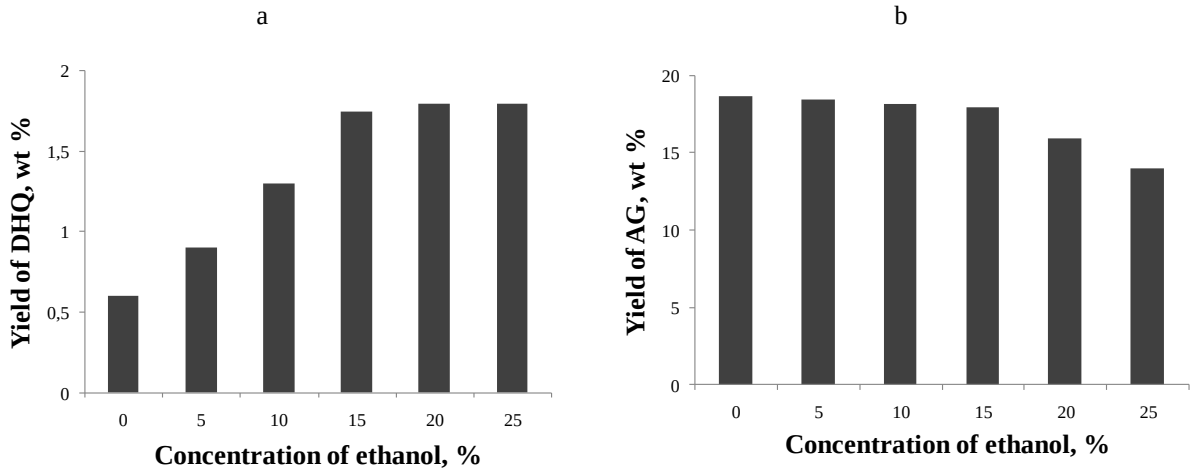


Fig.1 The yields of dihydroquercetin (a) and arabinogalactan (b) isolated from larch wood with ethanol-water solutions (extraction time 2 hours)

As follows from the obtained data, the optimum ethanol concentration which provides a high yield of DHQ (1.8 wt.%) and AG (18.0 wt%) corresponds to 15%.

It was established that a preliminary mechanical treatment of larch wood in a planetary mill for 2 min allows to shorten the time of the extraction of DHQ and AG from 2 to 0.5 hours without reducing their yields (Table.1).

Table 1 Influence of ethanol concentration on the yield and degree of extraction of DHQ and AG from larch wood, mechanically activated for 2 min*

Concentration of ethanol in water, %	Yield of DHQ from abs. dry wood, %	The degree of DHQ extraction, %	Yield of AG from abs. dry wood, %	The degree of AG extraction, %
0	0,52	26,0	18,7	94,0
5	0,83	41,5	18,5	93,0
10	1,3	65,0	18,3	92,0
15	1,81	90,5	18,0	90,4
20	1,78	89,0	16,9	84,9
25	1,82	91,0	15,1	76,0

*extraction time 0,5 h.

The structure of DHQ and AG isolated from larch wood were confirmed by FTIR and ^{13}C NMR methods.

Peroxide catalytic fractionation of larch wood

The promising approaches for wood biorefinery include, as a key stage, woody biomass fractionation on polysaccharides and lignin and their subsequent transformation to chemicals and liquid biofuels.

The known ways of lignocellulosic biomass fractionation can be divided into two groups. In one of them the cellulose and hemicelluloses are removed and the lignin remains as a rest, another includes methods in which the lignin is removed.

Reductive catalytic fractionation is the known way to separate lingocellulosic biomass into lignin-based soluble mono-, di- and oligomers while retaining most of the carbohydrates in the pulp (Van den Bosch et al. 2015; Schutyser et al. 2015; Anderson et al. 2016).

Catalytic oxidation of lignins by molecular oxygen in alkaline medium allows to separate lignocellulosic biomass on aromatic aldehydes (mainly vanillin and syringaldehyde) and cellulose (Tarabanko et al. 2017).

Peroxide catalytic oxidation of hardwood and softwood in acetic acid – water medium enables to achieve the effective separation of wood biomass components on microcrystalline cellulose and soluble products from lignin and hemicelluloses (Kuznetsov et al 2008, 2009, 2015).

In earlier works, the authors proposed to carry out the catalytic fractionation of larch wood on cellulose and soluble lignin in a "hydrogen peroxide-acetic acid-water" medium at temperatures of 120-130 ° C and increased pressure in the presence of catalysts H_2SO_4, H_2MoO_2 and $Fe_2(MoO_4)_3$ (Kuznetsov et al. 2008; Kuznetsova et al. 2005; Kuznetsova et al 2005). In recent studies the authors demonstrated the possibility an effective catalytic fractionation of aspen wood (Kuznetsov et al. 2013), birch wood (Garyntseva et al. 2015), fir wood (Kuznetsov et al. 2017) on microcrystalline cellulose and soluble lignin under mild conditions (temperature 100 ° C, atmospheric pressure). This was achieved by reducing the contribution of diffusion limitations of the delignification process when the hydromodule and the size of wood particles were decreased and the intensive mixing of the reaction medium was used. The high catalytic activity in the peroxide delignification of birch wood and abies wood at mild conditions demonstrated the suspended catalyst TiO_2 (Garyntseva et al. 2015; Kuznetsov et al. 2017).

In this study, the peroxide delignification process, catalyzed by TiO_2 was used for fractionation on MCC and soluble products the larch wood from which the DHQ and AG were removed. The successful replacement the dangerous H_2SO_4 catalyst and the expensive Mo catalyst on non-toxic and non-corrosive TiO_2 catalyst in peroxide fractionation of extracted larch wood under mild conditions was demonstrated. The optimal process conditions providing a high yield of cellulose with low content of residual lignin were determined.

To optimize the process of extracted larch wood peroxide fractionation in the presence of TiO_2 catalyst the influence of temperature, concentrations of hydrogen peroxide and acetic acid, liquid/wood ratio, time on the dynamics of lignin removal from wood was studied.

The increase of temperature from 70 °C to 100 °C, concentrations of H_2O_2 from 3 wt% to 6 wt%, CH_3COOH from 15 wt% to 35 wt% and LWR from 5 to 15 reduces significantly the content of residual lignin and of hemicelluloses in the cellulosic product (Table 2). But at the same time the yield of cellulosic product is decreased. The oxidative destruction of lignin, hemicelluloses and the amorphous part of cellulose in wood is accelerated when delignification temperature increased from 70 to 100 °C.

Delignification of larch wood at 70 °C during 4 h gives 60.2 wt% yield of cellulosic product containing 68.4 % of cellulose and 24.2 % of lignin. When raising the temperature to 100 °C, the yield of cellulosic product decreased to 44.2 wt%. The maximum content of cellulose in the product (93.1 %) was detected after 4-hour delignification of larch wood at 100 °C. Under such conditions, the residual lignin was actually absent in this sample and hemicelluloses amount was 5.8 %.

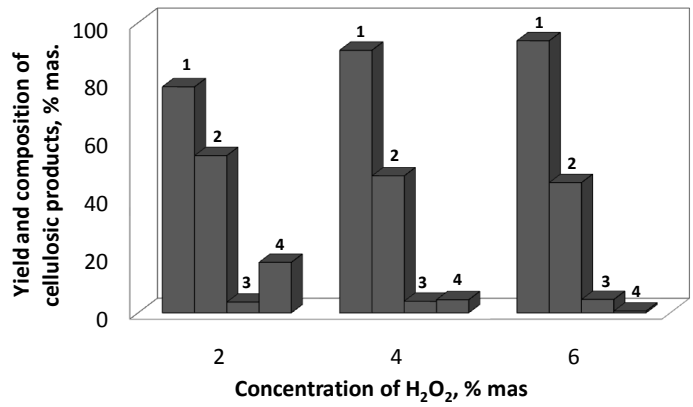
Table 2 Impact of delignification temperature on the yield and composition of cellulosic product obtained from extracted larch wood (CH_3COOH 25 wt%, H_2O_2 5 wt%, LWR 15, TiO_2 1 wt%)

Temperature, °C	Time, h	Yield of cellulosic product, wt%*	Composition of product, wt%**		
			Cellulose	Hemicellulose	Lignin
70	1	63,6	64,7	8,1	26,7
70	2	61,8	66,6	7,6	25,3
70	3	61,0	67,5	7,0	25
70	4	60,2	68,4	6,9	24,2
80	1	63,4	64,9	8,2	26,4
80	2	59,9	68,7	8,1	22,7
80	3	57,3	71,9	7,9	19,7
80	4	56,0	73,5	6,5	19,5
90	1	58,2	70,8	6,9	21,8
90	2	56,6	72,7	6,4	20,4
90	3	53,5	77,0	6,3	16,2
90	4	48,9	84,1	5,9	9,5
100	1	53,5	77,0	6,5	16
100	2	45,0	91,5	6,0	2
100	3	44,6	92,3	5,9	1,3
100	4	44,2	93,1	5,8	0,6

* on abs.dry wood, ** on abs.dry product

The influence of H_2O_2 concentration on cellulosic product yield and its composition was studied at 100 °C (Fig. 2). In the presence of 2.0 wt% of H_2O_2 the yield of cellulosic product is 77.9 wt%, but it has a rather high content of residual lignin (17.4 %). When the concentration of H_2O_2 increases, the content of residual lignin reduces, but the yield of cellulosic product is reduced simultaneously.

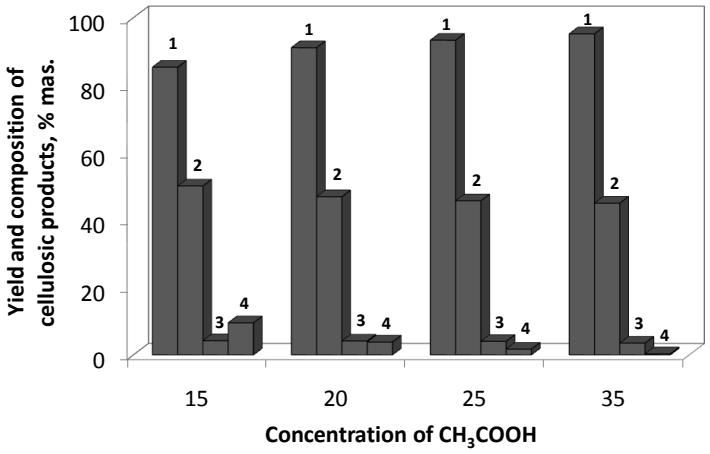
At the high H_2O_2 concentration, the oxidation of wood carbohydrates occurs along with the oxidation of lignin. According to the data obtained, the optimum concentration of H_2O_2, corresponding to the high yield of cellulosic product (near 45 wt% on a.d.w.) and low lignin content in the cellulosic product (0.6 – 4.5 wt% on a.d.p.) is 4–6 wt% (Fig. 2).



1 – cellulose, 2 – yield, 3 – hemicelluloses, 4 – lignin

Fig. 2 Impact of concentration of H_2O_2 on the yield and composition of cellulosic products obtained from extracted larch wood (CH_3COOH 30 wt%, 1 % TiO_2 catalyst, 100 °C, time 4 h)

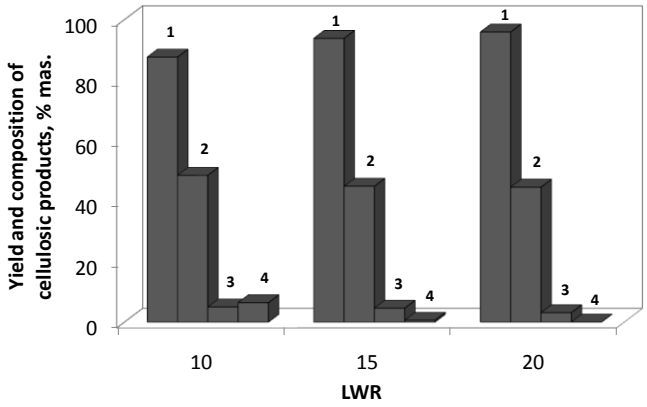
The increase of acetic acid concentration in reaction mixture decreases the yield of cellulosic product along with the reduction in residual lignin content (Fig. 3). While acetic acid concentration was increased from 15 to 35 wt%, the yield of cellulosic product decreased from 50.1 up to 45.0 %. Simultaneously, the content of cellulose in cellulosic product significantly increased from 85.3 up to 95.2 %. The concentration of acetic acid has also a strong influence on the residual lignin content. Its amount reached 9.5 % in the presence of 15 % wt of acetic acid and was lowered to 0.3 % when 35 % wt acetic acid was used. Experimental data presented in Fig. 3 show that the optimum concentration of acetic acid is nearly 25 wt% This concentration allows to reach the rather high yield of cellulosic product (45.7 wt%) with high amount of cellulose (93.3 %) and low content of residual lignin (1.7 wt%).



1 – cellulose, 2 – yield, 3 – hemicelluloses, 4 – lignin

Fig. 3 Impact of concentration of CH_3COOH on the yield and composition of cellulosic products obtained from extracted larch wood (H_2O_2 6 wt%, 1 % TiO_2 catalyst, 100 °C, time 4 h)

The value of the liquid/wood ratio (LWR) also allows controlling both the yield and composition of cellulosic products (Fig. 4). At liquid/wood ratio of 15–20 they have low content of residual lignin. The reduction in LWR to 10 increases both the amount of cellulosic product (48.5 %) and residual lignin concentration (6.4 %). A possible reason is a hindered diffusion of lignin oxidation products from wood to solution at low LWR. As a result, the small molecules of lignin oxidative fragmentation are re-condensed to so-called pseudo lignin (Hu et al. 2012). According to obtained data an optimal LWR value for studied process of larch wood delignification is equal to 15.



1 – cellulose, 2 – yield, 3 – hemicelluloses, 4 – lignin

Fig. 4 Impact of LWR on the yield and composition of cellulosic products obtained from larch wood (H_2O_2 6 wt%, CH_3COOH 30 wt%, 1 % TiO_2 catalyst, 100 °C, time 4 h)

The kinetic study of larch wood peroxide catalytic delignification in the temperature range 70–100 °C was accomplished. The variation of lignin concentration in the cellulosic product was used for calculating the rate constants of delignification process. It was found that the process of peroxide delignification of larch wood in the presence of TiO_2 catalyst is described by the first order equations (Fig.5).

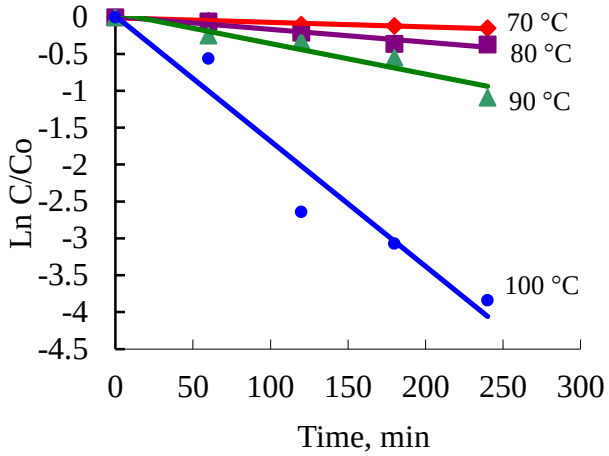


Fig.5 Dynamic of lignin isolation from extracted larch wood in the presence of 1 % TiO_2 catalyst (H_2O_2 5 wt%, CH_3COOH 25 wt%, LWR 15)

The calculated rate constants of larch wood peroxide delignification are presented in Table 3.

Table 3 Rate constants of extracted larch wood peroxide delignification (H_2O_2 – 6 wt%, CH_3COOH – 30 wt%, catalyst TiO_2 – 1 wt%, LWR – 15)

Temperature, °C	$k \cdot 10^{-4}$, c^{-1}
70	0,10
80	0,28
90	0,68
100	2,84

The activation energy of larch wood peroxide delignification process was determined using temperature dependence of the rate constants in Arrhenius coordinates (Fig. 6). The rather high value of activation energy (88 $kJ \cdot mol^{-1}$) points on the minor contribution of external diffusion limitations at the used conditions of larch wood peroxide delignification in the presence of TiO_2 catalyst.

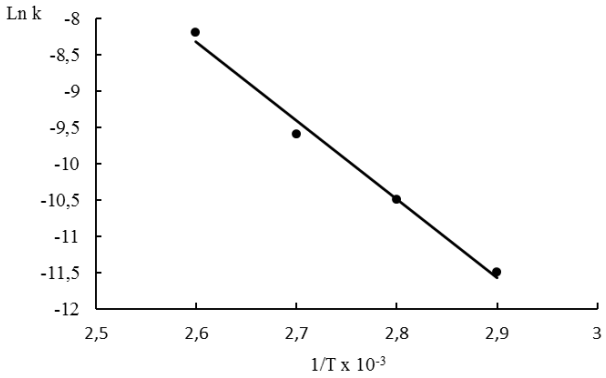


Fig. 6 Temperature dependence of rate constants of extracted larch-wood peroxide delignification (H_2O_2 6 wt%, CH_3COOH 30 wt%, LWR 15, 1 wt% TiO_2)

The similar kinetic parameters of peroxide delignification of aspen wood, birch wood and abies wood (Kuznetsov et al. 2017) (the first order equations, the comparable rate constants and values of activation energy) point to the identical mechanism of delignification processes in the presence of H_2SO_4 and TiO_2 catalysts.

The numerical optimization of the process of larch wood peroxide delignification in the presence of TiO_2 catalyst was carried out with the use of Statgraphic application software, according to earlier described procedure (Sudakova et al. 2013). The main purpose of the analysis was to find conditions for the most complete removal of lignin from wood, while maintaining a sufficiently high yield of cellulosic product.

As independent parameters, the following factors have been selected: X_1 – the H_2O_2 concentration in reaction solution, wt%; X_2 – liquid to wood ratio. The other process parameters were fixed: temperature 100 °C, concentration of acetic acid 30wt %; TiO_2 1wt %, time 4 h.

The following output parameters for optimization were selected: Y_1 – the cellulosic product yield, wt%; Y_2 – the cellulose content in the product, wt%; Y_3 – lignin content in the product, wt%.

Optimization was performed with the use of generalized parameter of optimization (W_a) which was calculated using the following equation:

$$Wa = \frac{\sum_{j=1}^{p} \delta j dj}{\sum_{j=1}^{p} \delta j}$$

where δ – the weight of the output parameter $0 \leq \delta_j \leq 1$; d_j – private utility function which was calculated using the following equation:

$$dj = \frac{\varphi_o(x) - y_j^{(-)}}{y_j^{(+)} - y_j^{(-)}}$$

Where $\varphi_0(x)$ – the response of output parameter at the point X; $y_j^{(+)}$, $y_j^{(-)}$ – the best and worst values of the output parameters, within the studied region.

Table 4 presents the data on conditions and results of experiments for the calculation of generalized parameter of optimization. When choosing weights δ, it was assumed, that the residual lignin content is the most important parameter. For this reason this parameter got the weight equal 1. The weights of such parameters as yield of cellulosic product and cellulose content in the product were choosing equal 0.5.

Table 4 Matrix for planning of the experiments on larch wood delignification, the results of dispersion analysis, the utility functions and the generalized parameter of the optimization

Experimental number	X_1	X_2	Y_1	Y_2	Y_3	d_1	d_2	d_3	Wa
1	2	10	62,1	71,3	25,7	0,9526	0,0120	0,0280	0,2552
2	4	10	51,7	82,8	11,1	0,4053	0,4720	0,5560	0,4974
3	6	10	48,5	87,6	6,4	0,2368	0,6640	0,7440	0,5972
4	2	15	54,2	77,9	17,4	0,5368	0,2760	0,3040	0,3552
5	4	15	47,2	90,5	4,5	0,1684	0,7800	0,8200	0,7564
6	6	15	44,9	93,8	0,6	0,0474	0,9120	0,9760	0,7279
7	2	20	50,8	84,8	10,7	0,3578	0,5520	0,5720	0,5135
8	4	20	45,4	93,3	2,2	0,1556	0,8920	0,9120	0,6471
9	6	20	44,6	95,9	0	0,0316	0,9960	0,9989	0,7179
$Y^{(-)}$			44	71	25				
$Y^{(+)}$			63	96	0				
δ			0,5	0,5	1,0				

Table 5 shows the results of analysis on the influence of the main factors on the generalized parameter of optimization W_a.

Table 5 Analysis of variances for W_a.

Dispersion source	Sum of squares	df	F-Ratio	P-Value
A:X1	0,140791	1	26,87	0,0139
B:X2	0,0465873	1	8,89	0,0585
AA	0,0223943	1	4,27	0,1305
AB	0,00473344	1	0,90	0,4120
BB	0,011285	1	2,15	0,2385

Analysis of variances showed that the effect of both factors X_1 and X_2 on the generalized parameter of optimizationis statistically significant (P-Value less than 0.05 and the confidence levels above 95%).

As a result of mathematical processing the following regression equation was obtained:

$$Wa = -1{,}1927 + 0{,}3398X_1 + 0{,}1215X_2 - 0{,}0264X_1^2 - 0{,}0034X_1X_2 - 0{,}0030X_2^2$$

Response surface of the generalized parameter of the optimization is presented on Fig. 7.

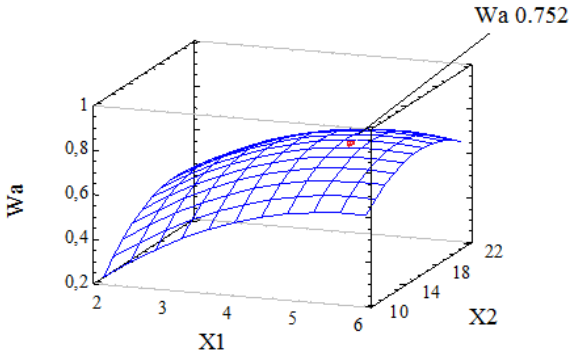


Fig. 7 Response surface of the generalized parameter (W_a) of the optimization of larch wood peroxide delignification with TiO_2 catalyst: X_1 – initial concentration of H_2O_2, X_2 – liquid to wood ratio

It was found, that the generalized parameter of the optimization is set to 0.752. This corresponds to the following optimal parameters of larch wood delignification process: temperature 100 °C, concentrations of H_2O_2 6.0 % wt. and of CH_3COOH 30 % wt., LWR 15, duration 4 h.

Cellulosic product obtained by peroxide fractionation of extracted larch wood at optimal condition with an yield 44.2 wt% has the following composition (wt%): cellulose 93.1, hemicelluloses 5.8, lignin 0.6. According to FTIR, XRD and SEM data the structure of this cellulosic product corresponds to that of commercial microcrystalline cellulose (Fig. 8, 9, 10).

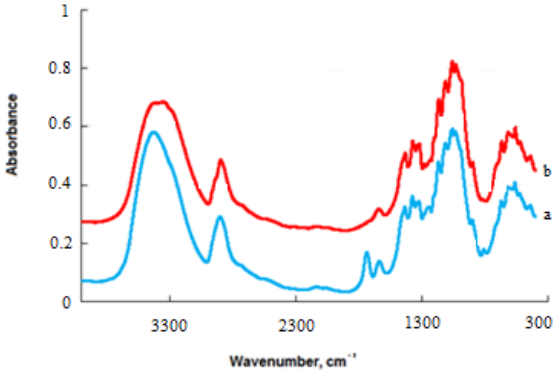


Fig. 8 FTIR spectra of cellulosic product from extracted larch wood (a) and of commercial microcrystalline cellulose Vivapur (b)

In FTIR spectrum of cellulosic product from larch wood the adsorption band, which corresponds to either the acetyl or uronic ester groups of hemicelluloses (Xiang et al. 2016) appears in the region 1700–1740 cm^{-1}. This fact indicates the presence of residual hemicelluloses in the cellulosic product from extracted larch wood.

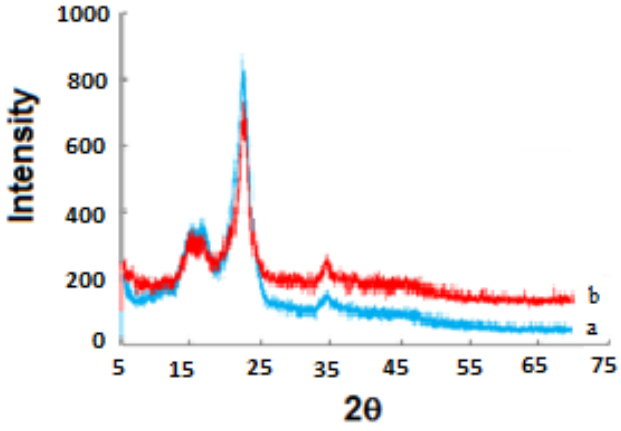


Fig. 9 Diffraction patterns of cellulosic product from extracted larch wood (a) and of commercial microcrystalline cellulose Vivapur (b)

Crystallinity index of cellulose from extracted larch wood, calculated as in paper (Park et al. 2010) is equal to 0.7.

a b

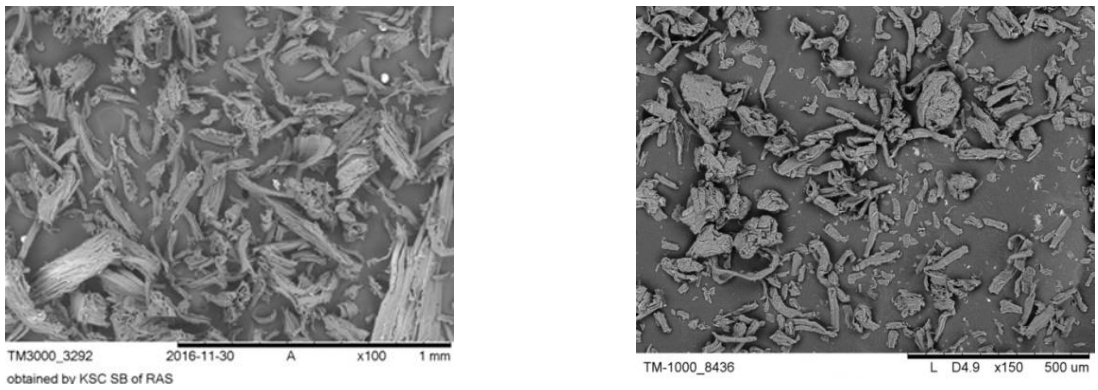


Fig 10 SEM images of cellulosic product from extracted larch wood (a) and of commercial MCC Vivapur 101 (b)

According to GC-MS data the soluble products of extracted larch wood peroxide fractionation contain only small amounts of aromatic compounds, indicating deep oxidation of phenylpropane units of lignin at studied process conditions. It is possible that the hydroxyl and peroxide radicals generated from H_2O_2 on the surface of TiO_2 catalyst can diffuse through the liquid reaction medium to the wood particles and to execute the oxidative destruction of lignin via homolytic mechanism (Kuznetsov et al. 2008).

Thus, the results of the study demonstrate the possibility of effective fractionation of extracted larch wood biomass into microcrystalline cellulose and soluble products from lignin under mild conditions (100°C, atmospheric pressure) in the medium "H_2O_2–CH_3COOH–H_2O–TiO_2 catalyst".

Development of the scheme of green biorefinery of larch wood

In our previous papers (Kuznetsov et al. 2013; Kuznetsov et al. 2013) it was suggested to use as a key process of biorefinery of low-grade wood the peroxide catalytic fractionation of wood biomass on polysaccharides and lignin.

Based on this approach the scheme of green biorefinery of larch-wood biomass is proposed which integrates the optimized processes of biomass fractionation on DHQ, AG, MCC and soluble lignin. Polysaccharides and lignin are further processed with obtaining of bioactive sulfated polysaccharides and nanoporous materials (Fig.11).

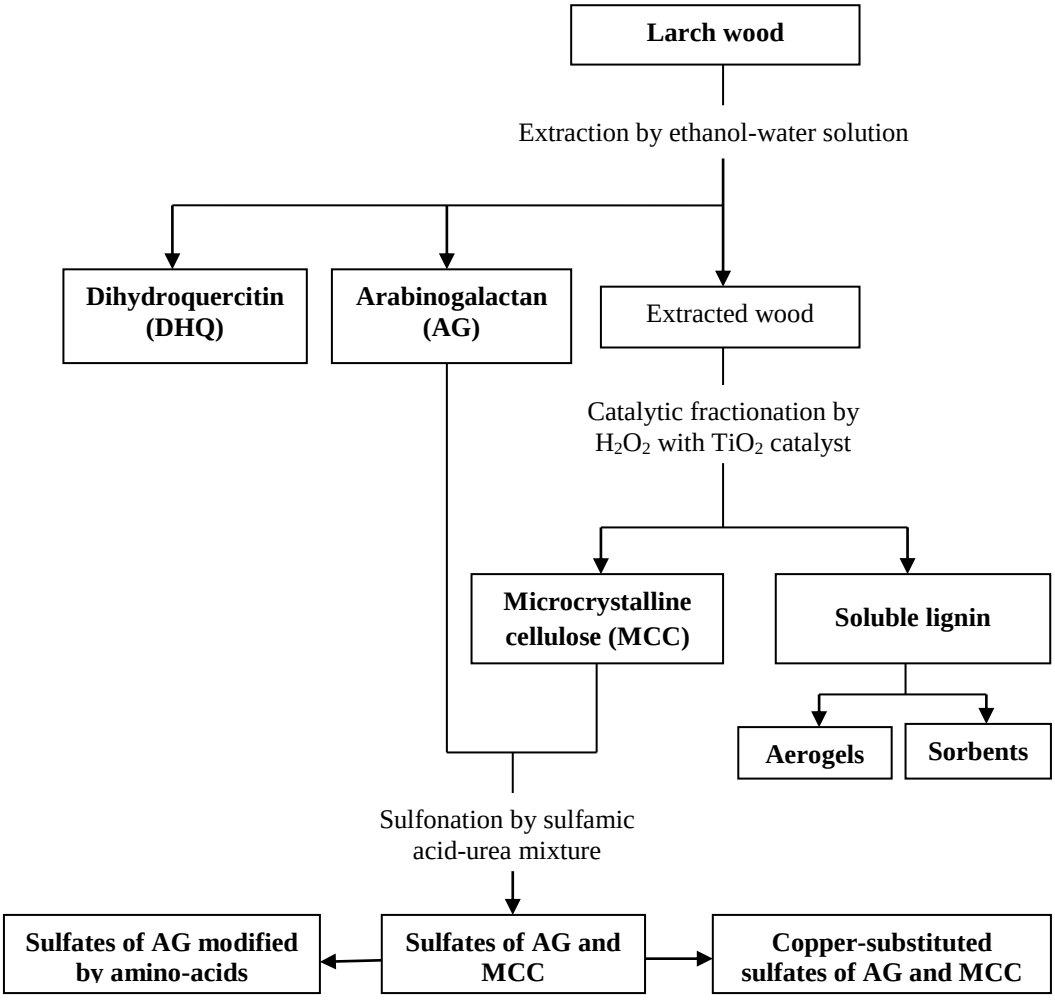
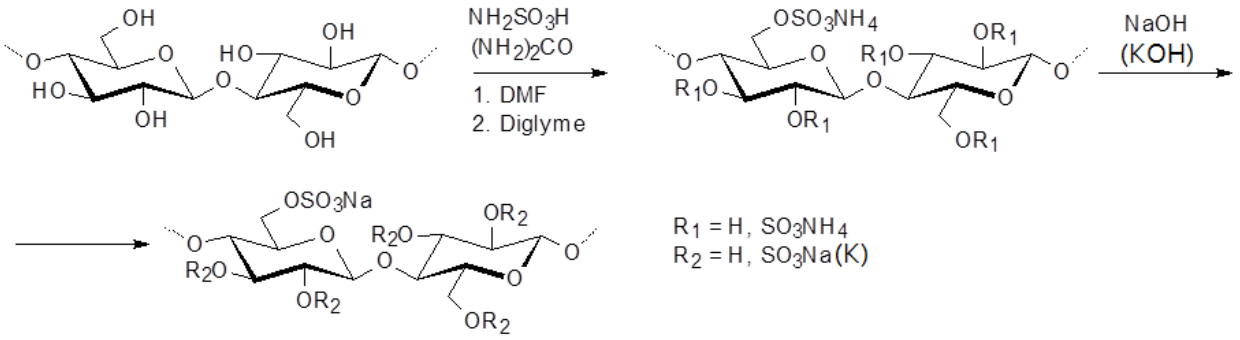


Fig. 11 Suggested scheme of green biorefinery of larch wood

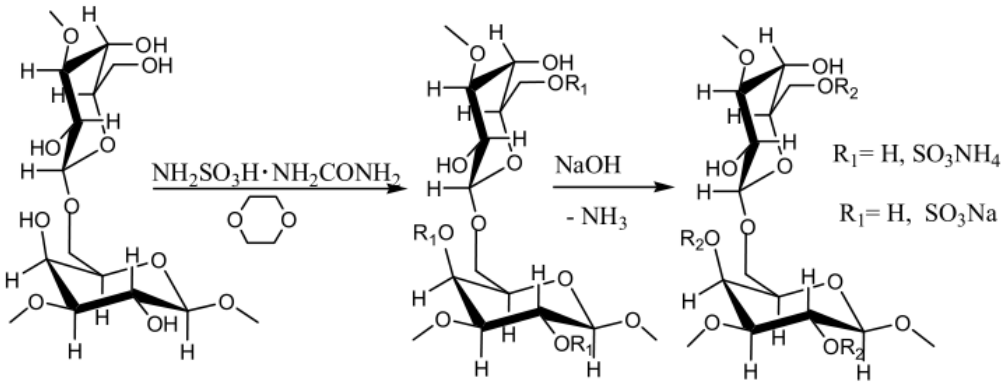
Described in this study new methods of DHQ and AG extraction from larch wood, catalytic peroxide fractionation the extracted wood on MCC and soluble lignin use such non-toxic agents, as water, ethanol, hydrogen peroxide, acetic acid.

For the synthesis of MCC and AG sulphates, we proposed yearly to use a low-toxic sulfamic acid and urea instead of dangerous and corrosive sulfating agents (Kuznetsov et al. 2015; Kuznetsov et al. 2017).

MCC sulfates are obtained as ammonium, sodium and potassium salts:



AG sulfates are obtained as ammonium and sodium salts (Kuznetsov et al. 2017):



Sulfated arabinogalactan can be used as water-soluble polymer for drug delivery.

On the basis of sulfated AG and MCC the new bioactive polymers, containing Cu^{2+} ions and amino-acids were synthesized by ion-exchange method.

The following scheme of obtaining the functional polymers of AG sulfates was used (Kuznetsov et al. 2017):

$$\text{1. R-SO}_3\text{Na} \xrightarrow{H^+} \text{R-SO}_3\text{H} + \text{Na}^+$$

$$\text{2. R-SO}_3\text{H} + \text{X} \longrightarrow \text{R-SO}_3^-\text{X}^+$$

$$\text{3. R-SO}_3^-\text{X}^+ + \text{AG-SO}_3^-\text{NH}_4^+ \longrightarrow \text{R-SO}_3^-\text{NH}_4^+ + \text{AG-SO}_3^-\text{X}^+$$

R – ion-exchange resin with $–SO_3H$-group, X – Cu^{2+}, amino-acids: glycine, ornithine, histidine, arginine, AG – arabinogalactan.

Procedure of functional polymers synthesis included the following steps:

- Substitution of Na^+ on H^+ in the resin
- Sorption of Cu^{2+} ions or amino-acids on SO_3H-groups of resin.
- Ion exchange of NH_4^+ groups of sulfated AG on Cu^{2+} cations or on protonated amino-acid.

Copper-containing sulfates of AG are the water-soluble powders which form the transparent films with green color after water evaporation. Analysis of EPR spectra showed that these polymers contain the isolated and interacting Cu^{2+} ions (Kuznetsov et al. 2017). The concentration of isolated Cu^{2+} ions decreases with the growth of copper content is sulfated AG. It was proposed that the isolated Cu^{2+} ions are fixed on AG areas with low concentration of sulfate groups, but and they form salt-like structures on the AG areas with high concentration of sulfate groups.

Ion-exchange method was firstly used for synthesis of water-soluble copper-containing sulfates of microcrystalline cellulose (Cu-MCS). The copper content in the obtained Cu-MCS samples is 12.6-14.1%. The absence of sodium in the obtained polymer shows complete substitution of sodium cations on the copper cations in the sodium salt of MCC sulfate. The structure of the copper-containing sulfates of MCC was studied by XRD, FTIR, EPR and AFM methods. It was shown by XRD, that Cu-MCS and the sodium salt of MCC sulfate had amorphous structure in contrast to the samples of the original MCC, with a high degree of crystallinity. FTIR spectrum of copper-containing MCC sulfate was similar to spectrum of sodium salt of MCC sulfate. According to EPR data there is a formation of copper-containing salt system with a pseudo-crystalline structure in the samples of Cu-MCS. As shown by atomic-force microscopy, the surface of the Cu-MCS films consists of homogeneous crystallites which have a spherical or slightly elongated form with average size of about 70 nm (Fig. 12). Surface of the film is homogeneous and it contains no impurities.

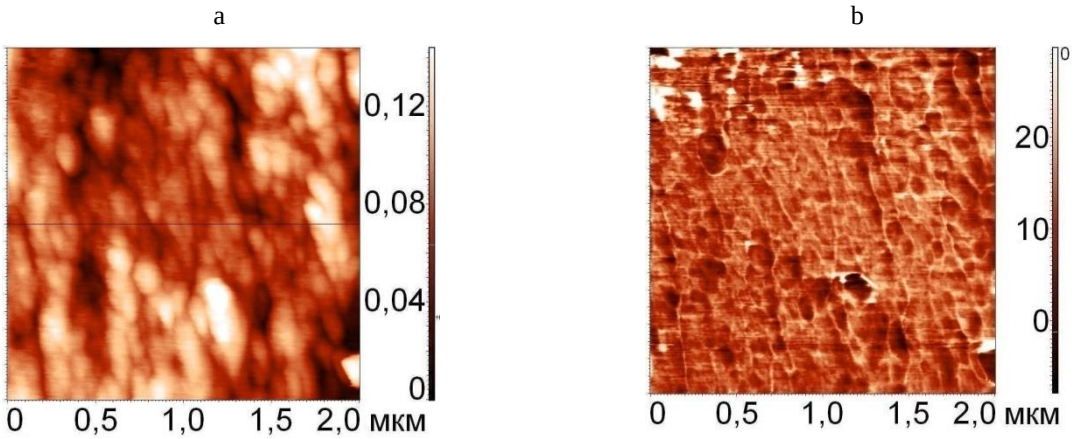
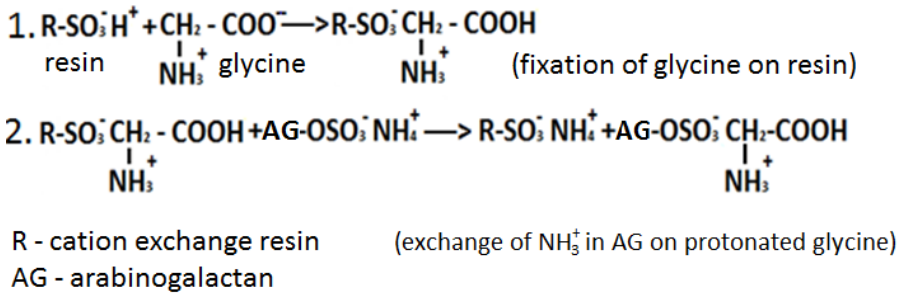


Fig. 12 AFM images of film of copper-containing MCC sulfate with Cu content 14.1 wt% (a – relief, b – phase contrast)

The water-soluble derivatives of sulfated arabinogalactan with amino acids glycine, ornithine, histidine and arginine were prepared by ion exchange method (Vasilyeva et al. 2016; Vasilyeva et al. 2016). From the analysis of FTIR spectra it is concluded that the resulting compounds contain the negatively charged sulfated arabinogalactan as an anion and the protonated forms of amino-acids – as a cations. In particular, the following two-stage scheme was used for glycine fixation on sulfated AG(Vasilyeva et al. 2016):



Synthesis of complexes of ornithine, histidine, arginine with sulfated AG was carried out by similar scheme (Vasilyeva et al. 2016; Vasilyeva et al. 2016).

The soluble lignin formed in the process of peroxide fractionation of larch wood is a light brown powder, its yield reached 9-9.5 wt% on abs. dry wood. Elemental composition of lignin (wt%): C – 46.58, H – 3.79. The simplest way of this lignin utilization is the obtaining of nanoporous materials.

The properties of enterosorbents obtained by alkaline treatment of peroxide lignins obtained from abies, aspen and birch wood were studied early by authors (Garyntseva et al. 2011). The optimum method of enterosorbents obtaining includes the treatment of peroxide lignins by the 0,4 % solution of $NaHCO_3$. The adsorption activity of obtained enterosorbents (34.7-39.0 % for iodine, 88.4-89.2 mg/g for methylene blue and 183.0-212.0 mg/g for gelatin) is similar to adsorption activity of commercial enterosorbent "Polyphepan". The yield of enterosorbents is 73.4–76.1 % on the weight of initial lignin. Their characteristics correspond to pharmacological standards. It can be expected that enterosorbents derived from larch wood lignin by the same way will possess by similar properties.

For obtaining from lignin the nanoporous carbon the method of thermal activation can be used (Kuznetsov et al. 2015). It was found that a partial gasification of wood and lignin in molten sodium and potassium hydroxides allow to obtain the active carbons with developed porous structure. The textural characteristics of active carbons, such as specific surface area, pore volume, macro-meso-micropores ratio, can be controlled by varying the nature of the alkali and its content in the mixture (Kuznetsov et al. 2015).

The other possible way of lignin utilization is the preparation of organic and carbon aerogels (Aegerter et al. 2011). They are highly porous materials combining a number of unique characteristics such as light weight, high surface area and adjustable mesoporosity. Carbon aerogels may be used as high surface area adsorbents or catalyst supports (Serp and Figueiredo 2009; Celzard et al. 2012; Szczurek et al. 2010; Job et al. 2006) and as electrodes for double-layer capacitor (Amaral-Labat et al. 2012; Calvo et al. 2014).

Yearly it was suggested to use lignin for preparation of highly porous organic tannin-lignin aerogels (Grishechko et al. 2013). So, the synthesis of new organic and carbon aerogels with the use of larch wood lignin is the promising area of its potentional application.

The obtained results in the field of larch biomass processing to valuable chemicals and functional organic materials open new opportunities in green biorefinery of larch wood.

Conclusion

The new approach to green biorefinery of larch-wood is described, which allows to obtain a more wide range of demanded products as compared to known methods of larch wood processing.

The suggested scheme of green biorefinery of larch-wood integrates the optimized methods of biomass fractionation on DHQ, AG, MCC, soluble lignin and subsequent processing of polysaccharides to bioactive polymers and lignin to nanoporous materials.

Described in the present paper the new methods of DHQ and AG extraction from larch-wood, peroxide catalytic fractionation of extracted wood on MCC and soluble lignin along with early described original methods of obtaining of bioactive sulfated polysaccharides and nanoporous materials from lignin use such non-toxic and less-toxic reagents, as water, ethanol, hydrogen peroxide, acetic acid, sulfamic acid, urea.

The developed green method of one-step obtaining of DHQ and AG based on the water-ethanol extraction of larch wood allow to obtain simultaneously the both compounds with high yields.

Based on kinetic studies and mathematical optimization of the process of extracted larch-wood peroxide delignification in the presence of green catalyst TiO_2 the optimal conditions of wood effective fractionation on MCC and soluble lignin were selected.

For green synthesis of bioactive functional polymers on the basis of sulfated MCC and AG we suggest to use non-dangerous sulfamic acid-urea mixture and methods of ion-exchange in water solutions.

Acknowledgements

The reported study was supported by Russian Science Foundation, grant N 16-13-10326.

This work is part of GDRI "Catalytic biomass transformation" between France and Russia.

References

Aegerter MA, Leventis N, Koebel MM (2011) Aerogels Handbook. Advances in sol-gel derived materials and technologies. Springer-Verlag, New York

Amaral-Labat G, Szczurek A, Fierro V, Stein N, Boulanger C, Pizzi A, Celzard A (2012) Pore structure and electrochemical performances of tannin-based carbon cryogels. Biomass and Bioenergy 39:274-282

Anderson EM, Katahira R, Reed M, Resch MG, Karp EM, Beckham GT, Roman-Leshkov Yu (2016) Reductive catalytic of corn of corn stover lignin. ACS Sustain Chem Eng 4:6940–6950

Babkin VA, Ostroukhova LA, D'jachkova SA, Svyatkin YuK, Babkin DV, Onuchin NA (1997) Waste-free complex processing of siberian and dahur larch biomass. Chemistry for Sustainable Development 45:105.

Babkin VA, Ostroukhova LA, Malkov YuA (2000) RF Pat. 2158598

Baryshnikov SV, Sharypov VI, Beregovtsova NG, Taran OP, Agabekov VE, Kuznetsov BN (2014) Thermal conversion of mechanically activated aspen-wood in sub- and supercritical ethanol medium. J. Sib. Fed. University. Chemistry **7:**455-463

Bessone M, Gallezot P, Pinel C (2014) Conversion of biomass into chemicals over metal catalysts. Chem Rev 114:827-1870

Calvo EG, Lufrano F, Arenillas A, Brigandi A, Menendez JA, Staiti P (2014) Effect of unequal load of carbon xerogel in electrodes on the electrochemical performance of asymmetric supercapacitors. Journal of Applied Electrochemisty 44:481-489

Celzard A, Fierro V, Amaral-Labat G (2012) Adsorption by Carbon Gels. In: Tascon JMD (ed) Novel Carbon Adsorbents. Elsevier, Oxford, pp 207-244

Cherubini F, Jungmier G, Wellish M et al. (2009) Toward a common classification approach for biorefinery systems. Biofuels, Bioproducts&Biorefining 172:534-546

Dagle VL, Smith C, Flake M, Albrecht KO, Gray MJ, Ramasamy KK, Dagle RA (2016) Integrated process for the catalytic conversion of biomass-derived syngas into transportation fuels. Green Chem 18:1880-1891

Davis SC, Hay W, Pierce J (2014) Biomass in the energy industry: an introduction. BP p.l.c., London

Ed de Long, Hidson A, Walsh P (2013) Biorefinery. Task 42. Report International Energy Agency Bioenergy

Garyntseva NV, Sudakova IG, Kuznetsov BN (2011) Properties of enterosorbents obtained from acetic acid lignins of abies, aspen and birch wood. J Sib Fed University Chemistry 4:121-126

Garyntseva NV, Sudakova IG, Kuznetsov BN (2015) Study of birch wood catalytic delignification by hydrogen peroxide at atmospheric pressure. J Sib Fed University Chemistry 8:422-429

Gavrilov AB (2009) RF Pat. 2372095

Gliozzi G, Innorta A, Mancini A, Bortolo R, Perego C, Ricci M, Cavani F (2014) Zr/P/O catalyst for the direct acid chemo-hydrolysis of non-pretreated microcrystalline cellulose and softwood sawdust. Applied Catalysis B: Environmental 145:24–33

Goellner EM, Utermoehlen J, Kramer R, Classen B (2011) Structure of arabinogalactan from Larix laricina and its reactivity with antibodies directed against type-II-arabinogalactans. Carbohydr Polym 86: 1739-1744

Grishechko LI, Amaral-Labat G, Szczurek A, Fierro V, Kuznetsov BN, Pizzi A, Celzard A (2013) New tannin-lignin aerogels. Ind Crop Prod 41:347-355

Horhammer HS, Treasure TH, Gonzalez RW, Heiningen ARP (2014) Larch biorefinery: technical and economic evaluation. Industrial and Engineering Chemistry Research 53:1206–1213

Hu F, Jung S, Radauskas A (2012) Pseudo-lignin formation and its impact on enzymatic hydrolysis. Bioresource Technol 117:7-12

Hu L, Linc L, Wu Z, Zhou S, Liu S (2015) Chemocatalytic hydrolysis of cellulose into glucose over solid acid catalysts. Applied Catalysis B: Environmental 174:225–243

Ishida K, Matsuda S, Watanabe M et al (2014) Hydrolysis of cellulose to produce glucose with solid acid catalysts in 1-butyl-3-methyl-imidazolium chloride ([bmIm][Cl]) with sequential water addition. Biomass Conv Bioref 4:323–331

Isikgor FH, Becer CR (2015) Lignocellulosic biomass: a sustainable platform for production of bio-based chemicals and polymers. Polym Chem 6:4497-4559

Job N, Heinrichs B, Lambert S, Pirard J, Colomer J, Vertruyen B et al. (2006) Carbon xerogels as catalyst supports: study of mass transfer. AIChE J 52:2663-2676

Kislitsin AN, Mal'chikov EL (2009) RF Pat. 2346941

Kuznetsov BN, Chesnokov NV, Ivanov IP, Veprikova EV, Ivanchenko NM (2015) Methods of porous materials obtaining from lignin and wood bark. J Sib Fed University Chemistry 8:232-255

Kuznetsov BN, Chesnokov NV, Yatsenkova OV, Sharypov VI (2013) New methods of heterogeneous catalysis for lignocellulosic biomass conversion to chemicals. Russian Chemical Bulletin 62:1493-1502

Kuznetsov BN, Kuznetsova SA, Danilov VG, Yatsenkova OV (2009) Influence of UV pretreatment on the abies wood catalytic delignification in the medium "acetic acid – hydrogen peroxide – TiO2. Reaction Kinetic and Catalysis Letters 97:295-300

Kuznetsov BN, Kuznetsova SA, Levdansky VA, Levdansky AV, Vasil'eva NYu, Chesnokov NV, Ivanchenko NM, Djakovitch L, Pinel C (2015) Optimized methods for obtaining cellulose and cellulose sulfates from birch wood. Wood Science and Technology 49:825-843

Kuznetsov BN, Sharypov VI, Grishechko LI, Celzard A (2013) Integrated catalytic process for obtaining liquid fuels from renewable lignocellulosic biomass. Kinetic and catalysis 54:344-352

Kuznetsov BN, Sudakova IG, Garyntseva NV, Djakovitch L, Pine C (2017) Kinetic studies and optimization of abies wood fractionation by hydrogen peroxide under mild conditions with TiO2 catalyst. React Kinet Mech Cat 120:81-94

Kuznetsov BN, Sudakova IG, Garyntseva NV, Djakovitch L, Pinel C (2013) Kinetic study of aspen-wood sawdust delignification by H_2O_2 with sulfuric acid catalyst under the mild conditions. Reac Kinet Mech Cat 110:271-280

Kuznetsov BN, Taraban'ko VE, Kuznetsova SA (2008) New Catalytic Methods for Obtaining Cellulose and Other Chemical Products from Vegetable Biomass. Kinetics and Catalysis 49:517-526

Kuznetsov BN, Vasilyeva NYu, Levdasky AV, Karacharov AA, Krylov AS, Mazurova EV, Bondarenko GN, Levdansky VA, Kazachenko AS (2016) Study by raman spectroscopy, xrd, sem, afm methods the sulfates of arabinogalactan obtained with the use of sulfamic acid. Khimiya Rastitel'nogo Syr'ya (Chemistry of plant raw materials) 4:43-48

Kuznetsov BN, Vasilyeva NYu, Levdasky AV, Maximov AV, Kazachenko AS, Skvortsova GP, Djakovitch L, Pinel C (2016) Synthesis and study of copper-containing polymers of sulfated arabinogalactan. . Khimiya Rastitel'nogo Syr'ya (Chemistry of plant raw materials) 4:49-55

Kuznetsova SA, Kuznetsov BN, Aleksandrova NB, Danilov VG, Zhizhaev AM (2005) Obtaining arabinogalactan, dihydroquercetin and microcrystalline cellulose using mechanochemical activation. Chemistry for Sustainable Development 13:261-268

Kuznetsova SA, Yatsenkova OV, Danilov VG, Kuznetsov BN (2005) Oxidative delignification of larch wood in acetic acid-hydrogen peroxide-water medium in the presence of H_2MoO_4 catalyst. Khimiya Rastitel'nogo syr'ya (Chemistry of Plant Raw Materials) 4:35-39

Li H, Fang Z, Smith Jr RL, Yang S (2016) Efficient valorization of biomass to biofuels with bifunctional solid catalytic materials. Prog Energy Combust Sci 55:98–194

Liu D, Chen EY-X (2014) Integrated catalytic process for biomass conversion and upgrading to C12 furoin and alkane fuel. ACS Catal 4:302–1310

Liu Y, Chen L, Wang T, Zhang Q, Wang C, Yan J, Ma L (2015) One-pot catalytic conversion of raw lignocellulosic biomass into gasoline alkanes and chemicals over $LiTaMoO_6$ and Ru/C in aqueous phosphoric acid. ACS Sustainable Chem Eng 3:1745–1755

Ma C, Yang L, Wang W, Yang F, Zhao C, Zu Y (2012) Extraction of dihydroquercetin from Larix gmelinii with ultrasound-assisted and microwave-assisted alternant digestion. Int J Mol Sci 13:8789–8804

Medvedeva EN, Babkin VA, Ostroukhova LA (2003) Arabinogalactan from larch—properties and usage perspectives. Khimiya Rastitel'nogo Syr'ya (Chemistry of plant raw materials) 1:27-37

Naik SN, Goud VV, Rout PK, Dalai AK (2010) Production of first and second generation biofuels: a comprehensive review. Renewable and Sustainable Energy Reviews 14:578-597

Pandey S (2015) Cellulases in conversion of lignocellulosic waste into second-generation biofuel. International Journal of Advanced Research 3:392-399

Park S, Baker JO, Himmel ME, Parilla PA, Jonson DK (2010) Cellulose crystallinity index: measurement techniques and their impact on integrating cellulose performance. Biotechnol Biofuels 3:10

Ramos LP (2003) The chemistry involved in the steam treatment of lignocellulosic materials. Quim Nova 26:863-871

Ravber M, Knez Z, Skerget M (2015) Isolation of phenolic compounds from larch wood waste using pressurized hot water: extraction, analysis and economic evaluation. Cellulose 22:3359–3375

Rowell RM (2012) Handbook of wood chemistry and wood composites, 2nd edn. CRC Press

Schutyser W, Van der Bosch S, Renders T, De Boe T, Koelewijn SF, Dewaele A, Ennaert T, Vikindereb O, Goderis B, Courtin CM, Sels BF (2015) Influence of bio-based solvents on the catalytic reductive fractionation of birch wood. Green Chem 17:5035-5045

Serp P, Figueiredo JL (2009) Carbon Materials for Catalysis. John Willey and Sons Inc, Hoboken

Serrano-Ruiz JC, Dumesic JA (2011) Catalytic routes for the conversion of biomass into liquid hydrocarbon transportation fuels. Energy Environ Sci 4:83-99

Sharypov VI, Beregovtsova NG, Baryshnikov SV, Zhizhaev AM, Vosmerikov AV, Kuznetsov BN (2015) The study of thermal conversion of mechanically activated aspen wood in the presence of high-silica zeolite catalyst. *J. Sib. Fed. University. Chemistry* **8:**190-201

Sixta H (2006) Handbook of pulp. Wiley-VCH Verlag GmbH & Co, Weinheim

Sjoöstroöm E, Alern R (1999) Analytical methods of wood chemistry. Pulping and papermaking. Springer-Verlag, Berlin

Sjostrom E (1993) Wood Chemistry- fundamentals and applications, 2nd edn. Academic Press, New Work

Sudakova IG, Garyntseva NV, Yatsenkova OV, Kuznetsov BN (2013) Optimization of aspen wood delignification by H_2O_2 with sulfuric acid catalyst. J Sib Fed University Chemistry 6:76-84

Szczurek A, Jurewicz K, Amaral-Labat G, Fierro V, Pizzi A, Celzard A (2010) Structure and electrochemical capacitance of carbon cryogels derived from phenol–formaldehyde resins. Carbon 48:3874-3883

Tarabanko VE, Kaygorodov KL, Skiba EA, Tarabanko NV, Chelbina YuV, Baybakova OV, Kuznetsov BN, Djakovitch L, Pinel C (2017) Processing pine wood into vanillin and glucose by sequential catalytic oxidation and enzymatic hydrolysis. J Wood Chem Technol 37:43-51

Troshina AV, Roshchin VI (2014) Hydrocarbons of neutral substances from the branch bark of Siberian larch. Russian Chemical Bulletin 63:2160–2168

Van den Bosch S, Schutyser W, Vanholme R, Drissen T, Koelewijn SF, Renders T, De Meester B, Huijgen WJJ, Dehaen W, Courtin CM, Lagrain B, Boerjan W, Sels BF (2015) Reductive lignocellulose fractionation into soluble lignin-derived phenolic monomers and dimers and processable carbohydrate pulps. Energy Environ Sci 8:1748–1763

Vasilyeva NYu, Levdasky AV, Kazachenko AS, Skvortsova GP, Kuznetsov BN (2016) Modification of sulfated arabinogalactan with amino acids by ion exchange method. J Sib Fed University Chemistry 9:20-28

Vasilyeva NYu, Levdasky AV, Kazachenko AS, Skvortsova GP, Kuznetsov BN, Djakovitch L, C. Pinel C (2016) Synthesis of sulfated arabinogalactan derivatives with histidine and arginine J Sib Fed University Chemistry 9:318-325

Xiang LY, Mohammed MAP, Baharuddin AS (2016) Characterisation of microcrystalline cellulose from oil palm fibres for food applications. Carbohydrate Polymers 148:11-20

Xu J, Xie X, Wang J, Jiang J (2016) Directional liquefaction coupling fractionation of lignocellulosic biomass for platform chemicals. Green Chem 18:3124–3138

Zhang X, Lei H, Zhu L, Qian M, Zhu X, Wu J, Chen S (2016) Enhancement of jet fuel range alkanes from co-feeding of lignocellulosic biomass with plastics via tandem catalytic conversions. Appl Energ 173:418–430

Zhang X, Lei H, Zhu L, Wei Y, Liu Y, Yadavalli G, Yan D, Wu J, Chen S (2015) Production of renewable jet fuel range alkanes and aromatics via integrated catalytic processes of intact biomass. Fuel 160:375–385

Zhang X, Lei H, Zhu L, Wu J, Chen S (2015) From lignocellulosic biomass to renewable cycloalkanes for jet fuels. Green Chem 17:4736–4747

Zheng Y, Pan Z, Zhang R (2009) Overview of biomass pretreatment for cellulosic ethanol production. Int J Agric Biol Eng 3:51–68